SYNTHESIS OF BROMOBENZOIC ACID DERIVED METAL COMPLEXES AND THEIR APPLICATIONS

M.Sc. Thesis

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DISCIPLINE OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE JUNE 2016

SYNTHESIS OF BROMOBENZOIC ACID DERIVED METAL COMPLEXES AND THEIR APPLICATIONS

A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree of Master of Science

> by SARTHAK MISHRA



DISCIPLINE OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE JUNE 2016



INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **Synthesis of bromobenzoic acid derived metal complexes and their applications** in the partial fulfillment of the requirements for the award of the degree of **MASTER OF SCIENCE** and submitted in the **DISCIPLINE OF CHEMISTRY, INDIAN INSTITUTE OF TECHNOLOGY INDORE**, is an authentic record of my own work carried out during the time period from JULY 2015 to JUNE 2016 under the supervision of Dr. Shaikh M. Mobin, Assistant professor, discipline of Chemistry, Indian Institute of Technology Indore. The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

SARTHAK MISHRA

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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July 2016

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DEDICATED TO.....

MY PARENTS AND SISTERS

For their endless support!

Abstract

The work enclosed in this thesis includes reaction of Dy(NO₃)₃.5H₂O which were carried out with bromo-benzoic acid (BBA) using 2, 2' bipyridine (2, 2'-bpy) as an ancillary ligand, in methanol and water (9:1) solvent system. At room temperature a 1-D polymeric chain $[Dy_2(BBA)_8(H_2O)]$.2, 2⁻ bpy.CH₃OH (2) was obtained whereas on heating at approx. 60° C for four hours a dimer [Dy₂(BBA)₆(2, 2' $bpy_2(CH_3OH_2)$ (1) along with some crystals of 2 were obtained. Both the complexes were characterized by elemental analysis, and single crystal XRD studies. The 1D polymeric complex 2 is present in hepta-coordination environment in which 2, 2²-bpy is present in the crystal lattice, whereas 1 is present in an octa-coordinated environment, generating square antiprism coordinaton geometry. The thermal studies suggest that 2 is more stable than 1. Additionally the reaction of Zn(CH₃COO)₂.2H₂O were also carried out with 4bromobenzoic acid (BBA) using 2, 2' bipyridine (2, 2'-bpy) as an ancillary ligand, in methanol and water (9:1) solvent system at 60° C forming a monomer $[Zn(BBA)_2(2, 2^2-bpy)]$ (3). Moreover application of **3** in catalyzing Henry reaction was also studied and characterized by GC-MS.

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NOMENCLATURE

θ	Angle
λ	Wavelength
α	Alpha
β	Beta
γ	Gamma
Å	Angstrom
δ	Delta
mm	Millimeter
π	Pi
mg	Milligram
d	Density
m	Meter
K	Kelvin
V	Volume

ACRONYMS

B.M	Bhor's magneton
МеОН	Methanol
4-BBA	4-Bromobenzoic acid
H ₂ O	Water
Вру	Bipyiridine
DCM	Dichloro methane
EPR	Electron paramagnetic resonance
GC-MS	Gas chromatography mass spectroscopy

CHAPTER 1.

INTRODUCTION

1.1 General introduction

The tendency of having a widely diverse coordination environment of transition metal and lanthanides metal complexes and also with the variation in the identities of coordinating ligands, synthesis of such metal complexes with desired molecular geometry can be realized and studied. These compounds often possess remarkable and unique application in the fields of spectroscopy, catalysis, electrochemical properties, molecular sensing [1-4], optical glasses, lasers. telecommunications, lighting and displays, hard-disk drives, security inks, counterfeiting tags, biosciences and medicine, magnetic resonance imaging [5], single-molecule magnets, and as spin qubits [6-8], to name but a few. Talking about the lanthanides metal ion Ln^{3+} it continues to attract considerable attention owing to the wide range of potential applications in fields as diverse molecular magnetism. The primary studies which ignites the discussion on the magnetic [9-10] and electronic properties of compounds containing lanthanide and transition metal ions date back to the beginning of the twentieth century. However, detailed investigation on these systems only began in the late 50s which helped to set up an appropriate theoretical framework for the analysis of their properties [11-15]. Considered as minor actors in transition metal chemistry for the very long time, they have now gained respect from coordination chemists who now are inserting them into them to sophisticated functional and poly functional molecules and materials.

The complexation of lanthanide and transition metal cations with various carboxylates based ligands in non-aqueous solution has been extensively studied in recent times [16, 17]. In the complexation studies by various aromatic monocarboxylate ligands [18, 19], in terms of the stability, it has been found that the stability constants of these

type of complexes correlate well with the acidity constants of the ligands, as also for the aliphatic monocarboxylate complexes [20,21]. Moreover for the metal complexes having ligands containing electron-withdrawing substituents such as Cl, Br and NO₂ on the aromatic benzene ring, there seems to be no charge polarization *via* resonance effects by the metal cations. It has been also found that the stabilities of these types of metal complexes are very much affected by the nature of the para-substituted group in the phenyl ring of the monocarboxylate ligands.

Monocarboxylate ligands containg electron withdrawing group at para position

Talking about the coordination number associated with the complexes of lanthanides and transition metal it has been found that in contrast to the transition metals coordination number six is not common in lanthanides and occur only with bulky ligands such as (2,6-dimethylphenyl)⁻ [22]. The most common coordination numbers are seven, eight and nine (Fig. 1) and these give variety of stereochemistry.



Fig.1 Bimetallic complex of lanthanum and lutetium [23]

Also lanthanide metals forms no complexes with π bonding ligands [24, 25], and the lack of it is due to the unavailability of the *f* orbitals for bonding while on the other hand transition metals forms very stable complexes with such ligands. It is difficult to explain the bonding in complexes with the high coordination number if one *s*, three *p* and all the *d* orbitals are used for bonding, this account for maximum coordination number of nine.

1.2 Transition metals in Catalysis

In recent days the development of environmental benign methodologies [26-28] has become one of the important tasks for the organic and inorganic chemists [29]. For fulfilling the needs of green chemistry, certain valuable challenges are remain, such as the replacement of expensive noble metals with cheap and affordable catalysts, increasing of reaction efficiency, using green reagents etc. Transition metal catalysts like Zn are cheap, abundant, and nontoxic. Therefore, the use of these catalysts instead of catalysts based on noble metals (Pd, Ir, Ru, etc.) is much more interesting and useful. Catalysts in general are the substances which alter the rate of the reaction without themselves getting changed. There are two types of the catalyst namely positive catalyst which increases the rate of the reaction and the negative catalyst which decreases the rate of the reaction. Transition metals are known for their remarkable involvement in the catalysis process. In a number of reaction transition metals and their oxides are used as a catalyst. Many of the transition metals such as iron, cobalt, nickel, platinum, chromium, manganese are the common catalyst used in various industries these days. Such as Ni in hydrogenation, Fe in Haber's process, V in contact process, Ti in Ziegler-Nata process. Transition metal have been very intensively involved in the catalysis process which can be attributed to the presence of the vacant *d*-orbitals, their ability to exhibit variable valancies and their tendency to form complex compounds. Hence use of transition metals as a catalyst now a day holds a very great importance in terms of industrial and sustainability aspects [30-39].

<u>1.3 What are Polymorphs?</u>

Polymorphs are one type of solid form. Other solid form types include solvates, hydrates, and amorphous forms. Solvates are crystalline materials made of the same chemical substance, but with molecules of solvent regularly incorporated into a unique molecular packing. Polymorphism is the ability of a solid material to exist in more than one form or crystal structure. Polymorphism can potentially be found in any crystalline material including polymers, minerals, and metals, and is related to allotropy, which refers to chemical elements. Polymorphism is relevant in the fields related of pharmaceuticals, pigments, dyestuffs, foods and explosives. Polymorphism is of three types packing, conformational and solvomorphism.

Taking about packing polymorphism it corresponds to the difference in crystal packing. Polymorphism can also result from the existence of different conformers of the same molecule in conformational polymorphism. In pseudo polymorphism there is a difference in the crystal types as the result of hydration or solvation. This is more correctly referred to as solvomorphism as different solvates have different chemical formulae. A classical example of the polymorph is the pair of minerals, calcite and aragonite, both forms of calcium carbonate.

1.4 Organization of the thesis

The aim of the project was to synthesis lanthanides and transition elements based metal complexes and to study their possible application in the areas of catalysis. The chapters includes in the thesis are

- <u>Chapter 2.</u> This chapter includes materials, instruments and the experimental procedure used to synthesize the metal complexes.
- <u>Chapter 3.</u> In this chapter results have been discussed which were obtained after the synthesis of the metal complexes.
- <u>Chapter 4.</u> This chapter concludes the described work and also looks for possible future scope and applications.

CHAPTER 2.

EXPERIMENTAL SECTION

2.1 Materials used

The commercially available starting materials $Dy(NO_3)_3.5H_2O$, $Zn(CH_3COO)_2.2H_2O$, 2,2'-bipyridine (bpy), 4-Bromobenzoic acid (BBA) and reagent-grade solvent methanol (MeOH), nitromethane (NM) and dichloromethane (DCM) were used as received. All the aldehydes used in catalytic reaction were also purchased from commercially available sources.

2.2 Instrumentation

Elemental analyses were carried out with a Flash 2000 elemental analyzer. Thermogravimetric analyses were performed on Metler Toledo thermal analysis system. The measurements were done at a heating rate of 5°C/min from 25 to 900 °C under flowing nitrogen environment. Single-crystal X-ray structural studies were performed on an Agilent Technology Supernova CCD diffractometer equipped with a low-temperature attachment. Gas chromatography–mass analysis was carried out on an Agilent HP-5890 instrument with an Agilent HP-5973 Mass Selective Detector (EI) and HP-5 capillary column (polydimethylsiloxane with 5% phenyl groups, 30 m, 0.25 mm i.d., 0.25 mm film thickness) by using helium carrier gas.

2.3 X-ray Crystallography

Data were collected at 150(2) K using graphite-monochromated Mo K α ($\lambda \alpha = 0.71073$ Å) and Cu K α ($\lambda \alpha = 1.54814$ Å). The strategy for data collection was evaluated using the CrysAlisPro CCD software. The data were collected by the standard $\varphi-\omega$ scan techniques and scaled and reduced using CrysAlisPro RED software. The structures were solved by direct methods using SHELXS-97 and refined by full-

matrix least squares with SHELXL-97 on F2.²¹ The positions of all of the atoms were obtained by direct methods. All non-H atoms were refined anisotropically. The remaining H atoms were placed in geometrically constrained positions and refined with isotropic temperature factors, generally 1.2Ueq of their parent atoms. All of the hydrogen-bonding interactions, mean-plane analyses, and molecular drawings were obtained using the Diamond program (version 3.3). The crystal and refinement data are summarized in Table 2, 3, 4, and selected bond distances and angles are shown in Table 5, 6, 7 in the appendix section.

2.4 Synthesis of Dy(II) complexes: 1 (Dimer) and 2 (Polymer)

Dy(NO₃)₃.5H₂O (0.438g, 1mmol), 4-bromobenzoic acid (0.210g, 1mmol) and 2, 2'-bipyridine (0.156, 1mmol) were dissolved in a mixture of methanol and water (9:1). The entire content was stirred and refluxed at 60^{0} C for 4 hours. The pink color solution was cooled to the room temperature and passed through filter paper (Whatman filter paper, 70 mm) in order to remove any unreacted materials. The filtrate was allowed to stand for crystallization at 298K. Upon very slow evaporation of the solvent two types of colorless crystals were formed (Needle shaped and block shaped) after ten days. The needle shaped crystals were characterized as **1** whereas block shaped crystals were characterized as **2**.

Interestingly, layering method (Water and methanol layers) also yielded both **1** and **2** whereas room temperature stirring of the whole contents for the 12 hours yielded only **2**.

Analysis calculated for **1** $[C_{32}H_{20}Br_3DyN_2O_7 (M_W = 946.72g/mol)]$: C,40.60 ; H,2.13; N,2.96. Found C, 40.42; H, 2.01; N,2.82. Analysis calculated for **2** $[C_{27}H_{15}Br_3DyNO_8 (M_W = 883.62g/mol)]$: C,36.70; H,1.71; N,1.59. Found C, 36.03; H, 1.56; N, 1.56.

SCHEME 1.



2.5 Synthesis of Zinc (II) complex: 3 (Monomer)

 $Zn(CH_3COO)_2.2H_2O$ (0.217g, 1mmol), 4-bromobenzoic acid (0.210g, 1mmol) and 2,2'-bipyridine (0.156, 1mmol) were dissolved in methanol and water (9:1). Few drops of ammonia solution were added to obtain a clear brown color solution. The entire contents were stirred and refluxed at $60^{0}C$ for 4 hours. The reaction mixture was concentrated and passed through filter paper (Whatman filter paper, 70 mm) in order to remove any unreacted materials. The filtrate was allowed to stand for crystallization at 298K. Upon very slow evaporation of the solvent colorless crystals of **3** were formed after seven days.

Analysis calculated for **3** $[C_{17}H_{12}BrN_2O_2Zn (M_W = 621.60g/mol)]$: C, 46.37 H, 2.59; N, 4.51. Found C, 46.01; H, 2.01; N, 4.08.

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SCHEME 2.



2.6. Catalytic activity of 3

Zn metal complexes have been very widely used in the catalytic reactions because they are cheap, abundant and non toxic in nature. Thus the catalytic activity of 3 was studied in Henry reaction.

Henry reaction is an organic reaction used to convert a nitroalkane with an α -hydrogen and an aldehyde or ketone to a β -nitro alcohol using a base catalyst which on dehydration gives nitroalkene.

SCHEME 3.



The catalytic behavior [40] of **3** was studied on Henry reaction, where Zn complex was supposed to act as a base catalyst.

10 mol% of **3** was added to the mixture of benzaldehyde (1mmol) and CH_3NO_2 (10ml), was refluxed and stirred at 353K for 14h. Nitromethane act as a reagent as well as solvent in the present reaction.

CHAPTER 3.

RESULTS AND DISCUSSION

1 and **2** are obtained by the reaction of $Dy(NO_3)_3.5H_2O$ with 4-BBA and 2,2'-bpy in 1:1 molar ratio in MeOH and H₂O solvent system (9:1) at 333 K (Scheme 1). The presence of bidentate ligands and tendency of lanthanides to accommodate high coordinating environment have led for the formation of high number complexes. These complexes were characterized by elemental analysis and single crystal X-ray studies. Their thermal stability was monitored by Thermogravimetric analysis.

3.1 Description of crystal structure and packing features of 1

 $[Dy_2(2,2'-bpy)_2(4-BBA)_6]$ (1) Crystallizes in triclinic, P₁ space group. Here, BBA coordinates to Dy(III) centers in two different manners *i.e.* monodentate and bridging. In the dimeric unit 1, Dy(III) is present in octa-coordination environment, bound with two nitrogen atoms of 2,2'-bpy, four oxygen atoms of four bridging BBA, one oxygen atom of terminal BBA and one methanol solvent molecule giving it a square antiprism coordination geometry (Fig. 2). The Dy–N bond distances are measured as Dy(1)-N(1) =2.586(7) and Dy(1)-N(2) =2.592(4) Å while the Dy–O bond distances fall in the range of 2.306(6)–2.446(6) Å.



Fig.2 Perspective view of 1 (hydrogen atoms have been omitted for clarity).

The packing diagram of **1** reveals the existence of weak intermolecular hydrogen bonding. The intermolecular hydrogen bonding involves bromine atom {Br(1)} of one molecule and pyridine molecule {C(9)-H(9)} of the neighboring molecule [Br(1)^{\cdots}H(9)-C(9) 3.002 Å]. With this intermolecular interaction **1** is extending in 1D layer (Fig. 3) and considering the vanderwalls radii of H and Br atoms (3.15 Å) this interaction seems to be a weaker one *[41]*. The 1D chain is extended to hydrogen bonded 2D network through Br atom of 4-BBA molecule of one layer and H atom of 4-BBA molecule of another layer. The 2D layer involves Br(3)^{\cdots}H(28)-C928) 3.015 Å, hence this also corresponds to weak interaction (Fig. 4) taking vanderwalls radii into consideration. The intermolecular interactions involved in the 2D layer is bit strong to that of involved in 1D layer considering the hydrogen involved in the H-bonding are aromatic in the former one.



Fig.3 Packing diagram showing weak intermolecular H-Bonded layer in 1.



Fig.4 Packing diagram showing intermolecular hydrogen bonded 2D layer in 1.

3.2 Description of crystal structure and packing features of 2

2 was obtained by the reaction of $Dy(NO_3)_3.5H_2O$ with 4-BBA and 2,2'-bpy in 1:1 molar ratio in MeOH and H₂O solvent system (9:1) at 298 K (Scheme 1). Complex **2** crystallizes in triclinic, P₁ space group. The asymmetric unit contains one Dy(III) ion, three 4-BBA ligands, one coordinated H₂O molecule, one 2,2'-bpy and methanol molecule.

As shown in Fig. 5, in the 1D-polymeric chain of **2**, the Dy(III) ion is coordinated by six oxygen atoms of six bridging 4-BBA molecules and one oxygen atom of water molecule, in a hepta-coordinated DyO₇ environment giving rise to pentagonal bipyramid coordination geometry. The Dy–O bond distances fall in the range of 2.297(6)– 2.405(6) Å which are similar to the bond distances measured for **1**. Here, 2, 2'-bpy and methanol solvent molecule are present in the crystal lattice.

Although 1 and 2 have same sort of ligands (*i.e.* 4-BBA and 2,2'-bpy) and solvent system (*i.e.* methanol and water) but the molecular structures of 2 differ from 1 by the coordination number (eight in 1, seven in 2); coordinated solvent molecule (methanol in 1, water in 2); and binding mode of 4-BBA (monodentate and bridging in 1, only bridging in 2).



Fig.5 Perspective view of 1D-Polymeric chain 2 (Hydrogen atoms have been omitted for clarity).

The packing diagram of **2** reveals that the 1D chain is extended to hydrogen bonded 2D layer through Br atom of 4-BBA of one layer and H atom of the 4-BBA of the other layer (Fig. 5). The 2D layer involves $Br(2)^{...}H(5)-C(5) = 3.030$ Å which corresponds to weaker interaction when the vanderwalls radii (3.15 Å) are taken into consideration. As 2, 2'-bpy is present in the lattice site and is not involve in any kind of secondary interactions, it has been omitted from the figure below.



Fig.6 Packing diagram showing intermolecular hydrogen bonded 2D layer in 2

3.3 Thermogravimetric analysis (TGA) of 1 and 2

Thermal study of complex **1** suggest weight loss of 24.5% between 50^{0} C to 300^{0} C which corresponding to the loss of coordinated MeOH, with molecules like 2, 2' bipyridyl and 4-BBA. Further loss above 300^{0} C may be attributed with to the release of other metal coordinated fragment (Fig. 6)

Thermal study of complex 2 suggest weight loss of 20% between 50° C to 30° C which corresponding to the loss of guest molecules like MeOH

and 2,2' bipyridyl also for the coordinated 4-BBA . Further loss above 300^{0} C can be attributed to the release of other metal coordinated polymeric fragment. TGA study also suggests that **2** more stable than **1** (Fig.7)



Fig. 7 TGA curve of 1



Fig.8 TGA curve of 1D-Polymeric chain 2

3.4 Description of crystal structure and packing diagram of 3

3 was obtained by the reaction of $Zn(CH_3COO)_2.2H_2O$ with 4bromobenzoic acid and 2,2'- bipyridine in 1:1 molar ratio in MeOH and H₂O solvent system (9:1) at 333 K (Scheme 2).

3 crystallize in triclinic, P_1 space group. In the lattice two monomeric units of **3** are present. The asymmetric unit of $[Zn(4-BBA)_2(2,2'-bpy)]$ contains one Zn(II) ion, two 4-BBA ligands, and one 2,2'-bpy. As shown in Fig. 8, the Zn(II) ion is coordinated by four oxygen atoms from two 4-BBA molecules and two nitrogen of 2,2'-bpy in an hexacoordinated ZnO₄N₂ environment giving rise to a distorted octahedral coordination geometry. The Zn–O bond distance s fall in the range of 1.968(4) – 2.556(5) Å.

In **3**, 4-BBA binds to the metal center in a bidentate manner which is different than **1** (monodentate and bridging), and **2** (bridging).



Fig. 9 Perspective view of 3 (hydrogen atom have been omitted for clarity).

Packing diagram of **3** reveals presence of intermolecular H-bonding between 4-BBA of two different molecules. The intermolecular interaction involve $O(3)^{...}H(21)-C(21) = 2.422$ Å, $O(1)^{...}H(20)-C(20) =$ 2.480 Å, $O(4)^{...}H(7)-C(7) = 2.434$ Å, $O(2)^{...}H(6)-C(6) = 2.407$ Å between the 4-BBA molecule of each monomeric unit. With these intermolecular interaction **3** is extending in 1D layer (Fig. 9). The 1D chain is extended to hydrogen bonded 2D network which involve $O(1)^{...}H(45)-C(45) = 2.422$ Å, $O(5)^{...}H(11)-C(11) = 2.521$ Å, $O(8)^{...}H(14)-C(14) = 2.514$ Å between 4-BBA of one layer and 2,2'bpy of the other layer.



Fig.10 Packing diagram showing intermolecular hydrogen bonded 1D layer in 3.



Fig.11 Packing diagram showing intermolecular hydrogen bonded 2D layer in 3.

3.4 Thermogravimetric analysis of 3

Thermo gravimetric analysis of complex **3** suggest weight loss of 24.5 % between 50° C to 300° C which corresponding to the loss of coordinated MeOH, with molecules like 2,2'bipyridyl and 4-BBA. Further loss above 300° C can be attributed with uncertainty to the release of other metal coordinated fragment (Fig.11).



Fig.12 TGA curve of Monomer 3.

3.5 Catalytic application of 3 in Henry reaction

Henry reaction also referred as nitro-aldol condensation reaction is a carbon bond formation reaction. Here nitroalkane condense with aldehydes and ketones to form β nitro-alcohols. The Henry reaction is a very useful technique in organic chemistry because of their synthetic utility in corresponding products, as they can be easily converted to other useful synthetic intermediates. These conversions include dehydration to form nitroalkenes, oxidation of the secondary alcohol to yield α -nitro ketones, or reduction of the nitro group to yield β -amino alcohols.

The catalytic behavior of **3** was studied on Henry reaction. [Zn(4-BBA)₂(2, 2'-bpy)] (10 mol%), benzaldehyde (1mmol) were added to 10ml of CH₃NO₂ and refluxed at 353K for 14h. The progress of the reaction was monitored by thin layer chromatography (TLC). After 14h the reaction samples were taken for GC-MS analysis and the corresponding results were analyzed (Table 1).

SCHEME 4.



 Table 1.

 Products and analysis of Zn complex Catalyzed Henry reaction







Zn complex **3** was found to catalyze the Henry reaction. Catalytic reactions were performed on aromatic aldehydes and the best results were obtained on 4-hydroxy benzaldehyde and benzaldehydes where the conversion into nitroalkene was observed to be 90% and 70% respectively with 80-90% selectivity. Some decent results were also obtained with hetro-cyclic compounds like furfural aldehyde and 2-thiophenecarboxoaldehyde where 90% and 60% conversion was observed. In addition aromatic aldehydes containing electron withdrawing groups at para, meta and ortho positions were also tolerable and gave good yield of the corresponding nitroalkene. Some cases very high selectivity was observed inspite of having very low yield such as 4-bromobenzaldehyde, 1,4-benzaldehyde and 4-methlybenzaldehyde with selectivity of 55%, 90% and 60% respectively.

CHAPTER 4.

CONCLUSION AND FUTURE WORK

Three new metal complexes, two of Dy(III) and one of Zn(II) were synthesized and characterized with 4-BBA and 2, 2'-bpy as the ligands. While the reaction of Dy(NO₃)₂.5H₂O yielded an octa and hepta coordinated dimeric and polymeric complexes, respectively, the reaction of Zn(CH₃COO)₂.2H₂O yielded a hexa coordinated monomer. The notable thing in the case of Dy(III) metal complex was, when the reaction was carried out at room temperature the complex formed was polymeric whereas when the same reaction was refluxed at 60° C the complexes formed were both dimer(1) and polymer (2). Also the reaction by layering method gave both 1 and 2. The packing in all the three complexes were also studied. It was observed that Dy(III) complexes were forming 1D and 2D packing through weak H-bonding between bromine and hydrogen while the monomeric complex of Zn(II) is extending in both dimension through strong H-bonding between hydrogen and oxygen. In the thermal analysis polymeric complex was found to be more stable than that of dimeric. Moreover the catalytic behavior of Zn(II) complex in catalyzing Henry reaction was studied and the product analysis was done by GC-MS.

Talking about the application of Dy(III) metal complex in single molecular magnets (SMM), it is yet to be explored. Molecular magnetism is a relatively recent section of magnetism which is one of the greatest fields of research and lot of work has now being carried out focusing on magnetism and lanthanides. The magnetic moment observed in the case of Dy(III) ion is 6.4-7.7 BM and this makes its complexes very much interesting for the study of SMM. Also the catalytic behavior of Dy(III) have been very less studied so far so its catalytic application in the oxidation reaction is also an area which is yet to be studied.

APPENDIX

Table 2. Crystal and structure refinement data of 2.

Empirical formula	$C_{27}H_{15}Br_3DyNO_8$
Formula weight	883.63
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system,	Triclinic, P-1
Space group	
	a = 9.0578(4) A alpha = 73.523(4) deg
Unit cell dimensions	b = 12.030(6) A beta = 79.372(4) deg.
	c = 14.144(6) A gamma = 81.005(4) deg
Volume	1443.87(11) A ³
Z, Calculated density	2,2.032 Mg/m ³
Absorption coefficient	6.787 mm ⁻¹
F(000)	868
Crystal size	0.25 x 0.23 x 0.21 mm
Theta range for data	3.06 to 25.00 deg
collection	
Limiting indices	-10<= h<=10, -14<=k<=14, -16<=l<=16
Refinement method	Full-matrix least-squares on F ²
Max. and min.	0.3298 and 0.2817
transmission	
Final R indices	R1 = 0.0495, wR2 = 0.1452
[I > 2 sigma (I)]	

Empirical formula	$C_{32}H_{20}Br_3DyN_2O_7$
Formula weight	946.73
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space	Triclinic, P-1
group	
	a = 10.7225(5) A alpha = 62.721(5) deg.
Unit cell dimensions	b = 13.1140(7) A beta = 69.890(5) deg.
	c = 14.040(7) A gamma = 72.49(5) deg.
Volume	1623.27(14) A ³
Z, Calculated density	2, 1.937 Mg/m ³
Absorption coefficient	6.043 mm ⁻¹
F(000)	906
Crystal size	0.20x0.15x0.10 mm
Theta range for data	2.94 to 25.00 deg.
collection	
Limiting indices	-12<=h<=12, -15<=k<=15, -16<=l<=16
Reflections collected	1391 / 5708 [R (int) = 0.0737]
unique	
Completeness to $\theta =$	99.9 %
25.00	
Absorption correction	Semi-empirical from equivalents
Max./ min. transmission	0.5832 and 0.3778
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	5708 / 0 / 406

Table 3. Crystal and structure refinement data of 1.

Empirical formula	$C_{24}H_{16}Br_2N_2O_4Zn$
Formula weight	621.60
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	TRICLINIC, P-1
	a = 7.387(3) A alpha = 101.6(4) deg.
Unit cell dimensions	b = 15.91(8) A beta = 92.890(4) deg.
	c = 19.91(11) A gamma = 97.43(4) deg.
Volume	2268.96(14) A ³
Z, Calculated density	4, 1.820 Mg/m ³
Absorption coefficient	4.639 mm ⁻¹
F(000)	1224
Crystal size	0.25 x 0.22 x 0.21mm
Theta range data collection	2.91 to 25.00 deg.
Limiting indices	-8<=h<=8, -18<=k<=18, -23<=l<=23
Reflections collected / unique	19891 /7975 [R(int) = 0.0639]
Completeness to $\theta = 25.00$	99.9
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.5832 and 0.3778
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	7975 / 0 / 595

Table 4. Crystal and structure refinement data of 3.

Dy(1)-O(4)	2.306(6)
Dy(1)-O(7)	2.318(6)
Dy(1)-O(3)	2.329(6)
Dy(1)-O(5)	2.331(6)
Dy(1)-O(1)	2.353(6)
Dy(1)-O(6)	2.446(6)
Dy(1)-N(1)	2.592(7)
Dy(1)-N(2)	2.586(7)
O(4)-Dy(1)-O(7)	74.5(2)
O(4)-Dy(1)-O(3)	81.9(2)
O(7)-Dy(1)-O(3)	83.4(2)
O(4)-Dy(1)-O(5)	83.6(2)
O(7)-Dy(1)-O(5)	121.8(2)
O(4)-Dy(1)-O(1)	123.1(2)
O(7)-Dy(1)-O(1)	79.5(2)
O(3)-Dy(1)-O(1)	143.6(2)
O(5)-Dy(1)-O(1)	73.1(2)
O(4)-Dy(1)-O(6)	142.0(2)
O(7)-Dy(1)-O(6)	74.5(2)
O(3)-Dy(1)-O(6)	73.3(2)
O(5)-Dy(1)-O(6)	136.8(2)
O(4)-Dy(1)-N(1)	138.4(2)
O(7)-Dy(1)-N(1)	146.9(2)
O(3)-Dy(1)-N(1)	77.2(2)
O(5)-Dy(1)-N(1)	77.2(2)
O(1)-Dy(1)-N(1)	81.4(2)
O(4)-Dy(1)-N(2)	78.7(2)
O(7)-Dy(1)-N(2)	144.9(2)
C(11)-O(3)-Dy(1)	140.5(7)

Table 5. Bond distances(Å) and bonds angles(deg) of 1.

C(20)-Dy(1)	3.009(8)
O(1)-Dy(1)	2.329(5)
O(2)-Dy(1)	2.371(6)
O(3)-Dy(1)	2.295(6)
O(4)-Dy(1)	2.328(6)
O(5)-Dy(1)	2.309(6)
O(5)-Dy(1)#2	2.902(7)
O(6)-Dy(1)	2.297(6)
O(7)-Dy(1)	2.405(6)
Dy(1)-O(5)#2	2.902(7)
Dy(1)-O(5)-Dy(1)#2	100.8(2)
C(19)#1-O(6)-Dy(1)	138.1(6)
O(3)-Dy(1)-O(5)	156.4(3)
O(6)-Dy(1)-O(5)	91.5(2)
O(3)-Dy(1)-O(4)	125.7(2)
O(5)-Dy(1)-O(4)	75.5(2)
O(3)-Dy(1)-O(1)	89.8(2)
O(6)-Dy(1)-O(1)	147.6(2)
O(5)-Dy(1)-O(1)	80.3(2)
O(4)-Dy(1)-O(1)	73.6(2)
O(5)-Dy(1)-O(2)	126.2(2)
O(4)-Dy(1)-O(2)	76.7(2)
O(1)-Dy(1)-O(2)	85.1(2)
O(3)-Dy(1)-O(7)	75.3(2)
O(6)-Dy(1)-O(7)	72.3(2)
O(5)-Dy(1)-O(7)	81.4(2)
O(4)-Dy(1)-O(7)	138.9(2)
O(1)-Dy(1)-O(7)	75.5(2)

Table 6. Bond distance(Å) and bond angles(deg) of 2.

O(2)-Dy(1)-O(7)	143.2(2)
O(3)-Dy(1)-O(5)#2	116.79(19)
O(6)-Dy(1)-O(5)#2	142.0(2)
O(5)-Dy(1)-O(5)#2	79.2(2)
O(4)-Dy(1)-O(5)#2	67.2(2)
O(1)-Dy(1)-O(5)#2	68.2(2)
O(3)-Dy(1)-C(20)	94.1(2)
O(6)-Dy(1)-C(20)	138.9(2)
O(5)-Dy(1)-C(20)	103.4(2)
O(4)-Dy(1)-C(20)	72.4(2)
O(1)-Dy(1)-C(20)	73.4(2)
O(2)-Dy(1)-C(20)	23.5(2)
O(7)-Dy(1)-C(20)	147.1(2)
O(5)#2-Dy(1)-C(20)	24.3(2)

Table 7. Bond distance(Å) and bond angle(deg) of 3.

Zn(1)-O(4)	1.968(4)
Zn(1)-O(1)	2.071(4)
Zn(1)-N(2)	2.087(5)
Zn(1)-N(1)	2.100(5)
Zn(1)-O(2)	2.185(4)
Zn(1)-C(1)	2.455(6)
Zn(1)-C(18)	2.585(6)
Zn(2)-O(8)	1.966(4)
Zn(2)-O(5)	2.012(4)
Zn(2)-N(4)	2.076(5)
Zn(2)-N(3)	2.100(5)
Zn(2)-O(6)	2.318(5)
Zn(2)-C(25)	2.487(6)

O(4)-Zn(1)-N(2)	105.15(19)
O(1)-Zn(1)-N(2)	100.58(17)
O(4)-Zn(1)-N(1)	106.82(18)
O(1)-Zn(1)-N(1)	107.39(18)
N(2)-Zn(1)-N(1)	78.4(2)
O(4)-Zn(1)-O(2)	97.98(16)
O(1)-Zn(1)-O(2)	61.57(15)
N(2)-Zn(1)-O(2)	156.68(18)
N(1)-Zn(1)-O(2)	92.24(19)
O(4)-Zn(1)-C(1)	122.04(18)
O(1)-Zn(1)-C(1)	30.17(17)
N(2)-Zn(1)-C(1)	129.84(19)
N(1)-Zn(1)-C(1)	101.3(2)
O(2)-Zn(1)-C(1)	30.83(16)
O(4)-Zn(1)-C(18)	28.98(17)
O(1)-Zn(1)-C(18)	115.88(17)
N(2)-Zn(1)-C(18)	102.9(2)
N(1)-Zn(1)-C(18)	135.40(19)
O(2)-Zn(1)-C(18)	98.71(18)
C(1)-Zn(1)-C(18)	110.05(19)
O(8)-Zn(2)-O(5)	132.77(17)
O(8)-Zn(2)-N(4)	111.02(17)
O(5)-Zn(2)-N(4)	111.71(18)
O(8)-Zn(2)-N(3)	108.94(19)
O(5)-Zn(2)-N(3)	98.55(18)
N(4)-Zn(2)-N(3)	78.2(2)
O(8)-Zn(2)-O(6)	100.26(17)
O(5)-Zn(2)-O(6)	60.74(16)
N(4)-Zn(2)-O(6)	90.16(18)
N(3)-Zn(2)-O(6)	150.76(18)

O(8)-Zn(2)-C(25)	119.01(19)
O(5)-Zn(2)-C(25)	30.95(18)
N(4)-Zn(2)-C(25)	102.8(2)
N(3)-Zn(2)-C(25)	127.05(19)
O(6)-Zn(2)-C(25)	29.80(17)
C(1)-O(2)-Zn(1)	86.5(4)
C(18)-O(4)-Zn(1)	103.2(4)
C(25)-O(5)-Zn(2)	95.4(3)
C(25)-O(6)-Zn(2)	82.6(4)

GC-MS spectra of Zn Catalyzed Henry reactions









Fig.15 GC-MS spectra 3 (m/z peak at 179)



Fig.16 GC-MS spectra 4 (m/z peak at 183)

























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